Broadband electrical spectroscopy (BES) studies on hydroxide-conducting membranes

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Redox flow batteries (RFBs) are an innovative family of electrochemical energy conversion and storage devices which run by exploiting redox processes of species delivered to the system in a fluid form [1]. In general, the operation of RFBs is reversible, showing a high roundtrip efficiency (up to over 80%) and fast response times; very high energy capacities can be obtained (up to the MWh scale) [2]. For these reasons, RFBs are attracting a considerable attention from both academia and industry as an answer to the growing need to develop devices capable to store large amounts of electrical power, a fundamental requirement for the implementation of next-generation "smart grids" [3].

As of today a wide variety of RFB systems are under development, based on different redox chemistries. A common feature shared by most RFB families is that they include a membrane to separate the anodic and cathodic compartments, preventing the intermixing of the reactant species. At the same time the membrane must allow the selective migration of suitable ionic species, necessary to maintain the charge balance during the operation of the device [4]. Thus, the development of new ion-conducting membranes able to transport the desired charged species is one of the most important aspects of the research [5]. Furthermore, the complex interplay between the chemical composition, structure and conductivity mechanism of these innovative membranes is still poorly understood. Consequently, it is difficult to carry out a rational research effort to obtain membranes suitable for applications.

In this work a family of ion-conducting membranes based on poly (vinyl benzyl trimethyl ammonium)-*b*-poly (methylbutylene**)** [PVBTMA-*b*-PMB] block copolymers is considered. The copolymers include p-tolyl side groups; the latter are further functionalized with trimethyl ammonium groups neutralized by OH^- anions. Three different membranes are studied, labeled I, II and III. Each is characterized by a different degree of functionalization (DF) of the p-tolyl groups, as follows: I – DF = 42%; II – DF = 63%; III – DF = 81%. The electric response of the membranes in the completely hydrated form is studied by broadband electrical spectroscopy (BES). Results highlight a number of events, indicated as σ_1, σ_2, σ_3 and σ_4 in Figure 1, associated to different polarization phenomena occurring within the materials. This behaviour is typical of systems characterized by a complex multiphasic nanostructure, including more than one domain with different dielectric constants. The electric response also evidences some step changes as the temperature is varied, which point to significant reorganizations in the domain structure of the materials. These evidences are studied in detail, allowing to: (a) propose a comprehensive model for the long-range charge transfer in this family of materials; and (b) elucidate how the latter is correlated to the chemical composition and nanostructure of the samples.

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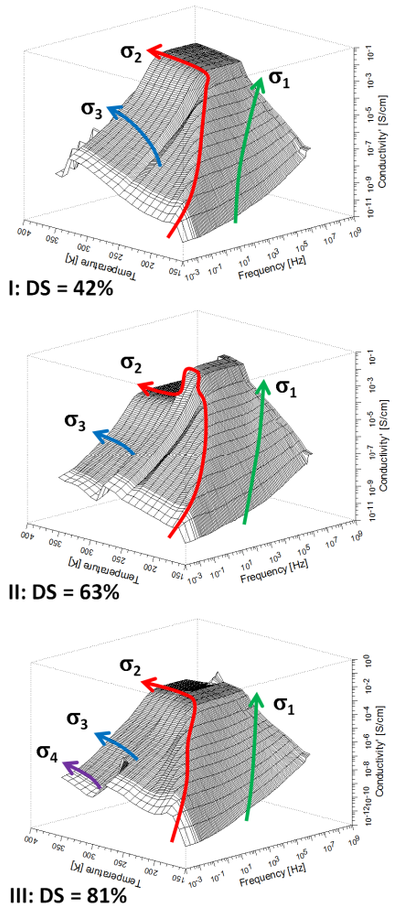

Figure 1. 3D surfaces of the real component of the conductivity as a function of temperature and frequency for the hydroxide-conducting membranes based on PVBTMA-*b*-PMB block copolymers.

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